Thermal recovery of the lattice damage in neutron-transmutation-doped InSe

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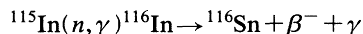
Positron-lifetime and transport measurements have been performed on neutron-transmutation-doped InSe in order to investigate the nature and recovery characteristics of the recoil-induced damage. The results show that the recovery is accomplished in two stages. The first, in the temperature interval $325 < T \leq 375$ K, is attributed to recombination of V_{In}-Sn_I close pairs into Sn_{In}. The second, observed for temperatures above ~475 K, is associated with annealing of other V_{In}-related defects.

I. INTRODUCTION

InSe is a layered semiconductor that is under active investigation because of the high anisotropy found in its electronic transport properties and its potential applications in photoconducting devices. Sn appears to be the most suitable donor impurity in InSe because it acts as a shallow donor and reduces the resistivity of the material without altering the electron mobility severely.[1,2] Neutron-transmutation doping (NTD) is a reproducible method for semiconductor doping.[3–5] It has been shown that InSe can be doped by neutron transmutation, yielding a very homogeneous and controlled concentration of Sn atoms.[6]

When InSe is exposed to thermal neutrons, the most naturally abundant In isotope (95.72%) transmutes into Sn via the following process:



$$^{115}\mathrm{In}(n,\gamma)^{116}\mathrm{In} \rightarrow {}^{116}\mathrm{Sn} + \beta^- + \gamma$$

The capture cross section of thermal neutrons by ^{115}In is 203 b vs 11.9 b for ^{113}In.[17] By far, the above is the most probable nuclear reaction in InSe: 99.70% of the nuclear reactions transmute In into Sn, $\simeq 0.26\%$ of the Se into As, and the remainder of the Se into Br or Kr, and the In into Cd. After finishing the transmutation processes, the transmuted atoms can very likely be displaced out of their original positions because of the γ and β^- recoils involved in the transmutation processes. The defects induced by these recoils, and by the residual flux of fast neutrons, appear to inhibit the electrical activity of the transmuted atoms and produce high resistivities.[3–5]

The electrical properties of NTD InSe has recently been investigated.[6] The results show that the transmuted Sn atoms become electrically active after annealing at ~725 K, reducing the resistivity of the material.

Positron-annihilation spectroscopy, as a technique sensitive to vacancies, is very useful to investigate the nature and charge state of those vacancy-type defects in compound semiconductors, which cannot be properly studied by means of the traditional techniques used to investigate defects in these materials. It is successfully applied to study the recovery of the radiation damage in compound semiconductors.[8,9] The positron-annihilation characteristics of as-grown and electron-irradiated samples of conventionally Sn-doped InSe have been recently investigated.[10,11] In this work, the thermal recovery of the recoil-induced damage in NTD InSe is investigated by positron lifetime and transport measurements.

II. EXPERIMENTAL

Undoped InSe single crystals were grown by the Bridgman method from a nonstoichiometric $In_{1.05}Se_{0.95}$ melt and exposed to a flux of thermal neutrons of 4×10^{11} n/cm^{2}s ($E < 0.04$ eV). The fast neutron flux on the sample was lower than 5% of the thermal neutron flux. The sample temperature during irradiation was 303 K. The samples for positron-annihilation experiments were irradiated up to a thermal neutron fluence of 6×10^{16} n/cm^2. The concentration of transmuted Sn in these samples was estimated to be 10^{17} cm^{-3}. After irradiation the samples were stored for 8 months prior to the positron-annihilation experiments in order to get low levels of radioactivity. The samples for transport measurements were irradiated at thermal neutron fluences of 1.5×10^{17} and 6.0×10^{17} n/cm^2; the transmuted Sn concentration in these samples was estimated to be 5×10^{17} and 2×10^{18} cm^{-3}, respectively.

Positron-lifetime measurements at low temperatures were performed on an irradiated monocrystalline slab ~1.5 mm thick set into a closed He-cycle cryostat. A ^{22}Na source deposited on a thin Ni foil was inserted into

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the sample through a slot made by cleaving along a basal plane. Afterwards, the sample was cleaved into two halves and isochronally annealed for 30 min in 50-K steps inside a quartz tube under flowing high-purity Ar gas. Positron-lifetime measurements at room temperature were done after each annealing with the ^{22}Na source sandwiched between the pair of samples. In addition, positron lifetime measurements at room temperature have been performed on reference samples of as-grown InSe single crystals.

The lifetime spectra were obtained using a spectrometer with a time resolution of 280 ps (full width at half maximum). The spectra were analyzed with a computer program subtracting two source corrections due to the contribution of positrons annihilating in the positron source. These corrections and the time resolution of the spectrometer were determined from the lifetime spectrum analyses of several reference samples. The number of counts accumulated in the spectra was typically more than 10^6 counts.

Resistivity and Hall effect (HE) measurements were performed on NTD samples 10–40 μm thick using electrical contact in the Van der Pauw configuration; ohmic contacts were made by soldering with high purity In. The measurements during thermal annealing were carried out in vacuum using a system implemented in the laboratory. The magnetic field strength for HE measurements was 0.6 T.

III. RESULTS AND DISCUSSION

All lifetime spectra were satisfactorily analyzed in terms of a single spectral component. Two-component analyses yielded inconsistent values with unacceptable variances or standard deviations. The spectra are characterized by the decay rate of their exponential term $\lambda=\tau^{-1}$, where τ is the positron lifetime in the samples. Figure 1 shows the temperature dependence of the positron lifetime in NTD InSe before thermal annealing. The results of the isochronal annealing experiments are shown in Fig. 2.

The NTD samples yielded a positron lifetime τ longer than the measured one on as-grown InSe, i.e., (307±3) ps; a value of (292±3) ps has been ascribed to the positron lifetime in the bulk, elsewhere.[11] This increase in τ

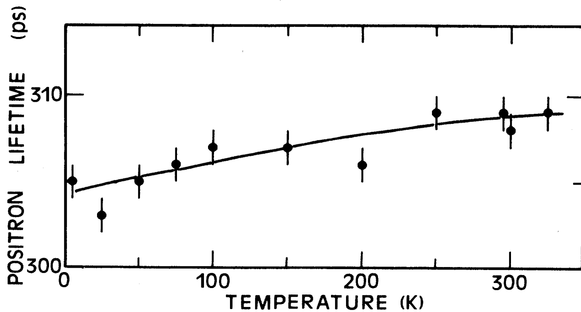

FIG. 1. Positron lifetime as a function of temperature in NTD InSe irradiated at a thermal neutron fluence of 6×10^{16} n/cm^2.

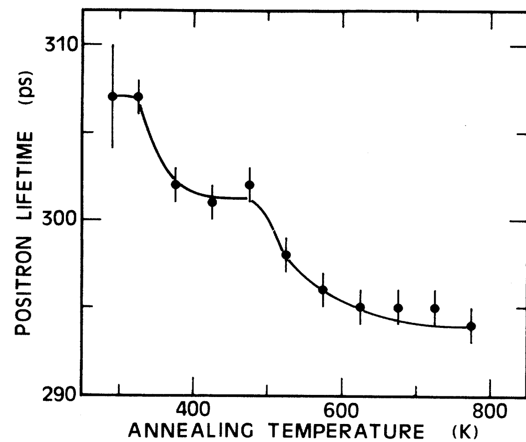

FIG. 2. Positron lifetime vs annealing temperature in NTD InSe irradiated at a thermal neutron fluence of 6×10^{16} n/cm^2.

has to be mostly due to the lattice damage induced by the recoils produced by the high energy γ and β^- particles involved in the transmutation processes of ^{115}In. At least, an important part of the positron traps would be $V_{\rm In}$-$\rm Sn_I$ close pairs created by the displacement of the transmuted atoms into interstitial positions, in addition to isolated $V_{\rm In}$ and $V_{\rm In}$-related complex defects; $V_{\rm In}$ denotes an In vacancy and $\rm Sn_I$ a Sn interstitial. Actually, the lifetime obtained from the single-component analyses should be interpreted as a weighted mean lifetime of positrons annihilating in the bulk and at the transmutation-induced defects. Therefore, the thermal annealing-induced decrease of τ would be evidence for annealing of the positron traps produced by the transmutation processes.

In regard to the charge state of the positron traps induced by NTD, the temperature dependence of τ shown in Fig. 1 can be interpreted as evidence for a neutral charge state. According to Puska *et al.*,[12] the low-temperature positron trapping rate for negatively charged defects increases strongly with decreasing temperature, while for neutral defects it is expected to be temperature independent. Thus, if the NTD-induced defects were negatively charged, an increase of τ with decreasing temperature would be expected instead of the observed temperature dependence.

The recovery of the positron lifetime starts after annealing above 325 K and appears to be accomplished at ~700 K, as seen in Fig. 2. The end of the recovery agrees with the complete activation of transmuted donor centers as revealed by the transport measurements. Its onset coincides with that observed in conventionally Sn doped InSe electron irradiated at room temperature and attributed to annealing of $V_{\rm In}$-related defects.[10] The temperature range is too wide to attribute the total recovery only to recombination of $V_{\rm In}$-$\rm Sn_I$ close pairs into $\rm Sn_{In}$. Moreover, Fig. 2 indicates that the recovery of τ is accomplished in two stages. The first in the interval $325<T\leq375$ K can be attributed to $V_{\rm In}$-$\rm Sn_I$ close-pair recombination. The second for temperatures above at

~475 K could be due to annealing of isolated centers V_{In} and/or V_{In}-Sn_{In} nonclose pairs, which would be more stable than the V_{In}-Sn_I close pairs. The capture recoil of ^{115}In followed by the decay recoils of ^{116}In, in combination with the fast neutron knock-on displacement can produce isolated centers V_{In} and V_{In}-Sn_{In} pairs. In conventionally Sn-doped InSe electron irradiated at 77 K a recovery stage starting after annealing above ~375 K has been attributed to annealing of centers V_{In}-Sn_{In}.[11] The discrepancy in the onset of the annealing stage attributed to centers V_{In} and/or V_{In}-Sn_{In} can be due to (a) the different characteristics of the structural damage induced by the electron irradiation at low temperature and by NTD, (b) differences in the concentration of defects, and (c) differences in the isochronal annealing treatments of the samples; treatments in Ref. 11 were performed in vacuum for 4 h in steps of 25 K.

The transport measurements yield results in agreement with the positron lifetime results. Figure 3 shows the Arrhenius plots of the electron concentration in two NTD InSe samples. Two activation energies are found in the investigated temperature range: 0.29 eV between 300 and 500 K and 1.14 eV above 500 K, showing that actually two different processes of defect annealing exist. As NTD samples at room temperature, prior to thermal treatment, have electron concentrations lower than 10^{13} cm^{-3}, then transmuted Sn atoms must be either in electrically nonactive configurations or be compensated by other NTD-induced defects with acceptor character such as In vacancies. During the first stage, an annealing process of low activation energy occurs increasing the electron concentration up to $\sim 10^{15}$ cm^{-3}. If it is accepted that this annealing stage corresponds to recombination of V_{In}-Sn_I close pairs, the transport measurements reveal that the concentration of these defects is only a small fraction of the total concentration of defects. The high activation energy process can then be attributed to diffusion of isolated Sn atoms, or Sn atoms in V_{In}-Sn_I nonclose configuration, through the lattice, so that their recombination with V_{In} centers results in new substitutional shallow donor centers Sn_{In} increasing the electron concentration by two orders of magnitude between 500 and 730 K. After annealing at 730 K, the electron concentration in the NTD samples at room temperature is almost the same as the estimated concentration of transmuted Sn atoms if this concentration is lower than 10^{17} cm^{-3}.[6]

The evolution of the electron mobility versus T^{-1} is shown in the inset of Fig. 3. Its temperature dependence is also consistent with the above interpretation of the annealing process. The low-electron mobility in the NTD samples before thermal treatment is due to a high concentration of ionized Sn atoms, whose electron scattering efficiency is enhanced by the fact that they are not screened because of the very low electron concentration. Thermal annealing reduces the concentration of ionized Sn atoms and increases the electron concentration as a result of the recombination between Sn interstitials and In vacancies. This produces an increase of the impurity screening and consequently of the electron mobility. As shown in the inset of Fig. 3, this increase also appears to take place in two stages.

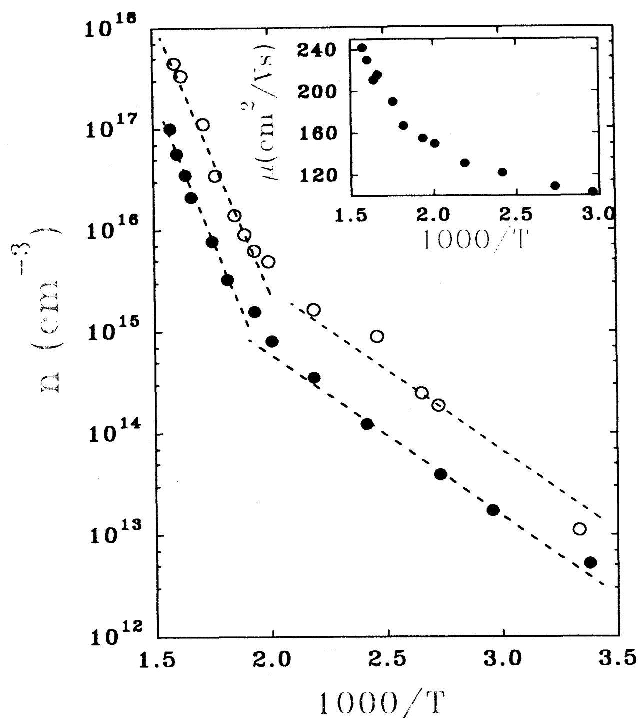

FIG. 3. Arrhenius plots of the electron concentration in two samples of NTD InSe with estimated Sn concentrations of 5×10^{17} (○) and 2×10^{18} cm^{-3} (●). The inset shows the electron mobility as a function of T^{-1} in the last sample.

IV. CONCLUSIONS

Our results reveal that the activation of the donor centers in NTD InSe is accomplished in two stages, the first by recombination of V_{In}-Sn_I close pairs and the second by annealing of the remaining In vacancies, i.e., centers V_{In} and/or V_{In}-Sn_{In} in nonclose configuration.

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